

**CHAPTER 4****IMPERFECTIONS IN SOLIDS****Introduction**

In the first three chapters we dealt with the properties of crystals under the assumption that, the atomic arrangements in crystals are perfectly regular and continuous throughout. In other words we dealt with ideal crystals. However, in actual crystals imperfections or defects are always present. **The term imperfection or defect is used to describe any deviation from the perfect periodic array of atoms in crystals.** No crystal is ideal. Imperfections or defects are always present in crystals. The study of these imperfections are important in the sense that many of the properties of crystals such as mechanical strength, ductility, crystal growth, dielectric strength, electrical and magnetic properties etc. are greatly affected by the imperfections in crystals.

The structural imperfections can be classified on the basis of their geometry as

- (i) point defects (zero dimensional defects)
- (ii) line defects (one dimensional defects)
- (iii) surface defects (two dimensional defects) and
- (iv) volume defects (three dimensional defects). We shall discuss these one by one.

**Point defects**

Point defects are also called zero dimensional defects since point is a zero dimensional object. Here we discuss only two defects: (i) vacancies and (ii) self interstitials.

## Vacancies

Vacancy is the simplest type of point defect in a crystal. This refers to a missing atom or vacant atomic site. Such defects may arise either from imperfect packing during the original crystallisation or from thermal vibrations of the atoms at high temperatures. In the latter case, when the thermal energy due to vibration is increased there is an increased probability that individual atom will jump out of their positions of lowest energy. For most crystals, this thermal energy is of the order of 1eV per vacancy. Vacancies may be single or two or more of them.

All crystalline solids contain vacancies and it is not possible to create a crystal without vacancy. The existence of vacancies is explained using principles of thermodynamics. The presence of vacancies increases the entropy of the crystal.

The equilibrium number of vacancies  $N_v$  for a given quantity of material is given by

$$N_v = N e^{\frac{-E_v}{kT}} \quad \dots \dots (1)$$

where  $N$  is the total number of atomic sites,  $E_v$  is the energy required for the formation of a vacancy,  $T$  is the absolute temperature in kelvin and  $k$  is the Boltzmann's constant. The value of  $k$  is  $1.38 \times 10^{-23} \text{ J/atom}$  or  $8.62 \times 10^{-5} \text{ eV/atom K}$ . For most of the

metals  $\frac{N_v}{N}$  is of the order of  $10^{-4}$ , when the temperature is below the melting point of the crystal.

$$\frac{N_v}{N} = 10^{-4}$$

or

$$N_v = 10^{-4} N$$

It implies that in 10,000 lattice sites there is only one vacancy.

In the vacancy there is no bonding, hence the value of mechanical strength of the crystal at that point is reduced.

### Example 1

The fraction of vacancy sites in a metal is  $1 \times 10^{-10}$  at  $500^{\circ}\text{C}$ . What will be the fraction of vacancy sites at  $1000^{\circ}\text{C}$ .

### Solution

We have

$$N_v = N e^{\frac{-E_v}{kT}}$$

$$\therefore \frac{N_v}{N} = e^{\frac{-E_v}{kT}}$$

$$10^{-10} = e^{\frac{-E_v}{kT}}$$

$$10^{10} = e^{\frac{E_v}{kT}}$$

Take natural log on both sides, we get

$$23.03 = \frac{E_v}{kT}$$

$$\begin{aligned} E_v &= 23.03 \times kT \\ &= 23.03 \times 8.62 \times 10^{-5} \times 773 \quad (\because T = 773\text{K}) \\ &= 1.53\text{eV}. \end{aligned}$$

Again

$$\begin{aligned} \frac{N_v}{N} &= e^{\frac{-1.53}{8.62 \times 10^{-5} \times 1273}} \quad (\because T = 1273\text{K}) \\ &= e^{-13.94} \\ &= 8.83 \times 10^{-7} \end{aligned}$$

**Example 2**

Calculate the fraction of atom sites that are vacant for copper at its melting temperature 1357K. Assume  $E_v = 0.90\text{ eV/atom}$ .

**Solution**

We have

$$N_v = N e^{\frac{-E_v}{kT}}$$

$$\frac{N_v}{N} = e^{\frac{-E_v}{kT}}$$

$$= e^{\frac{-0.9}{8.62 \times 10^{-5} \times 1357}}$$

$$= e^{-7.69} = 4.5 \times 10^{-4}$$

**Example 3**

Calculate the energy for vacancy formation in silver, given that the equilibrium number of vacancies at 800°C is  $3.6 \times 10^{13}\text{ cm}^{-3}$ . The atomic weight and density at 800°C for silver are 107.9g/mol and  $9.5\text{ gcm}^{-3}$ .

**Solution**

We have

$$N_v = N e^{\frac{-E_v}{kT}} \quad \dots\dots (1)$$

The number of sites,

$$N = \frac{N_A \rho}{A_{A_i}}$$

$$N = \frac{6.02 \times 10^{23} \times 9.5}{107.9}$$

$$N = 0.53 \times 10^{23}$$

Put the values of  $N_v$ ,  $N$  in eq (1), we get

$$3.6 \times 10^{17} = 0.53 \times 10^{23} \times e^{\frac{-E_v}{kT}}$$

$$\frac{3.6}{0.53} \times 10^{-6} = e^{\frac{-E_v}{kT}}$$

$$6.39 \times 10^{-6} = e^{\frac{-E_v}{kT}}$$

Take natural log on both sides, we get

$$-11.9 = -\frac{E_v}{kT}$$

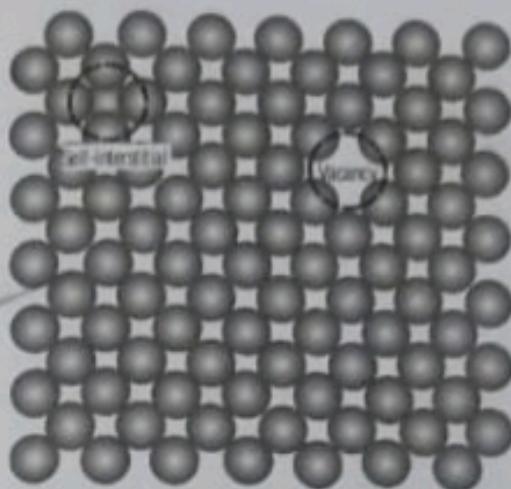
$$\therefore E_v = 11.9 \times kT = 11.9 \times 8.62 \times 10^{-5} \times 1073 \\ = 1.10 \text{ eV/atom.}$$

### Self interstitial defect

An interstitial defect is a type of point defect where an atom of the same or of a different type occupies an interstitial site in the crystal structure. When the atom is of the same type as those already present they are known as a self-interstitial defect.

Alternatively, small atoms in some crystals may occupy interstitial sites, such as hydrogen in palladium. Interstitial sites may exist in small concentrations in thermodynamic equilibrium. Interstitials can also be produced by bombarding a crystal with elementary particles having energy above the displacement threshold. The presence of interstitial defects can modify the physical and chemical properties of materials.

Two dimensional representations of a vacancy and a self-interstitial defect is depicted in figure 4.1.



**Figure 4.1:** Two-dimensional representations of a vacancy and a self-interstitial

### Impurities in solids

A pure crystal such as iron, silver, NaCl, brass etc., is not made up of one type of atom or atoms. Impurity atoms will always be present. This will result in crystalline impurity point defects such as substitutional and interstitial.

It is impossible to refine crystals in excess of 99.999%. At this level of purity it contains 0.001% of impurity. We can say that there are  $10^{22}$  to  $10^{23}$  impurity atoms will be present in one cubic metre of material. Most familiar metals are not 100% pure. Rather they are alloys, in which impurity atoms have been added intentionally to get specific characteristics to the material. ordinarily alloying is used in metals to improve mechanical strength and corrosion resistance. For example sterling silver is an alloy consists of 92.5% silver and 7.5% copper. Normally pure silver is highly corrosion resistant, but also very soft. Alloying with silver significantly increases the mechanical strength without depreciating the corrosion resistance appreciably.

The addition of impurity atoms will result in the formation of solid solution. With regard to alloys (solid solution) solute and solvent are terms that commonly used in analogy with liquid

solution. Solvent represents the element that is present in the greatest amount and solute represents the element present in a minor concentration.

### **Solid solution**

A solid solution is formed as the solute atoms are added to the solvent atoms.

The solid solutions are of two types. They are substitutional and interstitial.

### **Substitutional solid solutions**

These result from replacing the particle that should occupy a lattice site with a different particle.

For example substituting a  $K^+$  ion for a  $Na^+$  ion in  $NaCl$ . If  $Ca^{2+}$  ion is substituted for a  $Na^+$  ion, the second  $Na^+$  ion must leave the crystal so that it doesn't pickup an electric charge to maintain the electrical neutrality. There are several features of solute and solvent atoms that determine the degree to which solute dissolves in solvent.

#### **(i) Atomic size factor**

When the difference in atomic radii between the two atom types (solvent and solute) is less than about  $\pm 15\%$  appreciable amount of solute may be accommodated in this type of solid solution.

#### **(ii) Crystal structure**

For appreciable solid solubility the crystal structures for both atom type must be the same.

#### **(iii) Electronegativity**

The more electropositive one element and the more electronegative the other element, the greater is the likelihood that they will form an intermetallic compound instead of a substitutional solid solution.

#### **(iv) Valencies**

Other factors being equal, a metal will have more of a tendency

to dissolve another metal of higher valency than one of a lower valency.

For example a substitutional solid solution is formed for copper and nickel. This is because all four conditions required are met. The atomic radii for copper and nickel are 0.128 and 0.125 nm respectively. Thus first condition is fulfilled. Since both have same crystal structures the second condition is also met.

The third requirement is satisfied since their electronegativities are 1.9 and 1.8. The difference is very small. Finally the valency of copper is +1 and that of nickel is +2 hence tendency to dissolve is higher.

### Interstitial solid solutions

These are formed when impurity atoms (solute) fill the voids of the solvent atoms. For metallic materials that have relatively high atomic packing factors, their interstitial positions are relatively small. Consequently the atomic diameter of an interstitial must be smaller than the solvent atom to occupy the voids of solvent atoms. Normally, the maximum allowable concentration of interstitial impurity atoms is low (less than 10%). Even very small impurity atoms are ordinarily larger than the interstitial sites. The consequence is that impurity atoms produce some lattice strains to adjacent solvent atoms.

For example carbon forms an interstitial solid solution when added to iron. The maximum concentration of

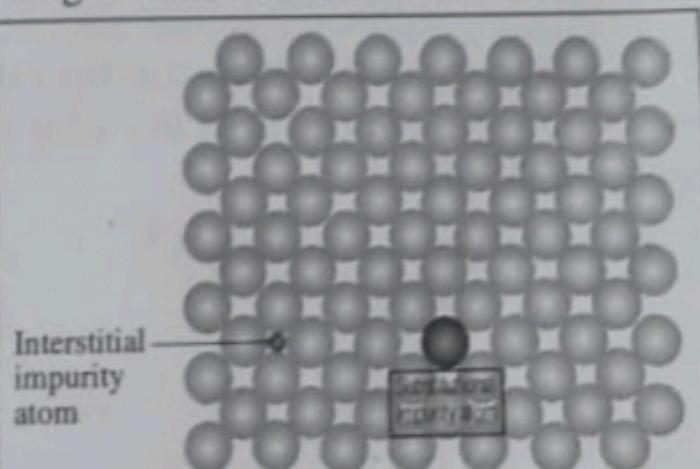


Figure : 4.2: Two-dimensional schematic representations of substitutional and interstitial impurity atoms

carbon is about 2%. The atomic radius of the carbon ( $0.071\text{nm}$ ) is much less than that for iron ( $0.124\text{nm}$ ).

A two dimensional schematic representations of substitutional and interstitial impurity atoms are shown in figure 4.2.

### Specification of composition

An alloy contains two or more elements. The percentage of the elements that occur in an alloy is usually expressed by the term composition or concentration. It can be done in two ways. One is in terms of mass percent the other one is in terms of atom percentage. **The mass percent is defined as the ratio of the mass of a particular element and the mass of the alloy.**

Suppose an alloy consists of two atoms 1 and 2 with masses  $m_1$  and  $m_2$ , respectively mass percentage of  $m_1$ ,

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100 \quad \dots\dots (1)$$

Similary, mass percent of  $m_2$ ,

$$C_2 = \frac{m_2}{m_1 + m_2} \times 100 \quad \dots\dots (2)$$

**The atom percent is defined as the ratio between number of moles an element present in the alloy to the total number of moles of the alloy.**

The atom percent of element 1,

$$n_{m_1} = \frac{m'_1}{A_1} \quad \dots\dots (3)$$

where  $m'_1$  denotes the mass of element 1 in grams and  $A_1$  is its atomic mass. Thus concentration in terms of atom percent is

$$C'_1 = \frac{n_{m_1}}{n_{m_1} + n_{m_2}} \times 100 \quad \dots\dots (4)$$

\*

similarly

$$C'_2 = \frac{n_{m_2}}{n_{m_1} + n_{m_2}} \times 100 \quad \dots\dots (5)$$

### Composition conversion

Suppose we want to convert from mass % to atom %, sometimes it is necessary.

#### Conversion from mass percent to atom percent

Consider two atoms 1 and 2 in an alloy. Let  $C_1$  and  $C_2$  be the mass percent of elements 1 and 2 respectively. Similarly  $C'_1$  and  $C'_2$  be the atom percent of elements 1 and 2 respectively.

Total mass of the alloy

$$M' = m'_1 + m'_2 \quad \dots\dots (6)$$

Prime is used to denote that mass is expressed in grams, we have

$$C'_1 = \frac{n_{m_1}}{n_{m_1} + n_{m_2}} \times 100$$

But  $n_{m_1} = \frac{m'_1}{A_1}$  and  $n_{m_2} = \frac{m'_2}{A_2}$

$$\therefore C'_1 = \frac{\frac{m'_1}{A_1} / 100}{\frac{m'_1}{A_1} + \frac{m'_2}{A_2}} \quad \dots\dots (7)$$

From eq (1), we get

$$C_1 = \frac{m'_1}{m'_1 + m'_2} \times 100$$

$$C_1 = \frac{m'_1}{M'} \times 100$$

or  $m'_1 = \frac{C_1 M'}{100}$  ..... (8)

Similarly  $m'_2 = \frac{C_2 M'}{100}$  ..... (9)

Substituting eq 8 and 9 in eq 7, we get

$$C'_1 = \frac{\frac{C_1 M'}{100 A_1}}{\frac{C_1 M'}{100 A_1} + \frac{C_2 M'}{100 A_2}} \times 100$$

$$C'_1 = \frac{\frac{C_1 M' / A_1}{A_1}}{\frac{C_1 M' / A_1}{A_1} + \frac{C_2 M' / A_2}{A_2}} \times 100$$

$$C'_1 = \frac{\frac{C_1 / A_1}{C_1 / A_1 + C_2 / A_2}}{\frac{A_1}{A_1 + A_2}} \times 100$$

or  $C'_1 = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$  ..... (10)

Using  $C'_1 + C'_2 = 100$

$$C'_1 = 100 - C'_2$$

Put this in eq (10), we get

$$100 - C'_2 = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

$$C'_2 = 100 - \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

$$C'_2 = 100 \left( 1 - \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \right)$$

$$C'_2 = \frac{C_2 A_1}{C_1 A_2 + C_2 A_1} \times 100 \quad \dots\dots (11)$$

### Conversion from atom percent to mass percent

From eq 10, we have

$$C'_1 = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100 \quad \dots\dots (12)$$

$$C'_1 A_1 = \frac{C_1 A_1 A_2}{C_1 A_2 + C_1 A_1} \times 100 \quad \dots\dots (13)$$

From eq 11, we have

$$C'_2 = \frac{C_2 A_1}{C_1 A_2 + C_2 A_1} \times 100 \quad \dots\dots (14)$$

$$C'_2 A_2 = \frac{C_2 A_1 A_2}{C_1 A_2 + C_2 A_1} \times 100 \quad \dots\dots (15)$$

Adding eq 13 and 15, we get

$$C'_1 A_1 + C'_2 A_2 = \frac{A_1 A_2 (C_1 + C_2)}{C_1 A_2 + C_2 A_1} \times 100$$

Using  $C_1 + C_2 = 100$ , we get

$$C'_1 A_1 + C'_2 A_2 = \frac{A_1 A_2 \times 100^2}{C_1 A_2 + C_2 A_1} \dots\dots (16)$$

$\frac{\text{Eq 13}}{\text{Eq 16}}$  gives

$$\frac{C'_1 A_1}{C'_1 A_1 + C'_2 A_2} = \frac{C_1}{100}$$

$$\therefore C_1 = \frac{C'_1 A_1}{C'_1 A_1 + C'_2 A_2} \times 100$$

Using this we can convert atom% to mass%.

Similarly,  $\frac{\text{Eq 15}}{\text{Eq 16}}$  gives

$$C_2 = \frac{C'_2 A_2}{C'_1 A_1 + C'_2 A_2} \times 100 \dots\dots (17)$$

#### Example 4

What is the composition, in atom percent of an alloy that consists of 92.5 mass% Ag and 7.5 mass% Cu.  $A_{\text{Ag}} = 107.87$  and  $A_{\text{Cu}} = 63.55$ .

**Solution**

Atom percent,

$$C'_1 = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

at% of Ag,

$$C'_{Ag} = \frac{C_{Ag} A_{Cu}}{C_{Ag} A_{Cu} + C_{Cu} A_{Ag}}$$

$$\left. \begin{array}{l} C_{Ag} = 92.5 \\ C_{Cu} = 7.5 \end{array} \right\} \text{given}$$

$$A_{Ag} = 107.87 \text{ g/mol}$$

$$A_{Cu} = 63.55 \text{ g/mol}$$

$$\therefore C'_{Ag} = \frac{92.5 \times 63.55}{92.5 \times 63.55 + 7.5 \times 107.87} \times 100$$

$$C'_{Ag} = \frac{5878.375}{6687.4} \times 100$$

$$C'_{Ag} = 87.9 \text{ at\%}$$

$$C'_{Ag} + C'_{Cu} = 100$$

$$C'_{Cu} = 100 - C'_{Ag} = 100 - 87.9$$

$$C'_{Cu} = 12.1 \text{ at\%}$$

**Example 5**

What is the composition, in mass percent of an alloy that consists of 5 at% Cu and 95 at% Pt.  $A_{Cu} = 63.55$ ,  $A_{Pt} = 195.08$ .

**Solution**

Mass percent

$$C_i = \frac{C'_i A_i}{C'_1 A_1 + C'_2 A_2} \times 100$$

$$C_{\text{Cu}} = \frac{C'_{\text{Cu}} A_{\text{Cu}}}{C'_{\text{Cu}} A_{\text{Cu}} + C'_{\text{Pt}} A_{\text{Pt}}} \times 100$$

$$C_{\text{Cu}} = \frac{5 \times 63.55 \times 100}{5 \times 63.55 + 95 \times 195.08}$$

$$C_{\text{Cu}} = \frac{31775}{317.75 + 18532.6}$$

$$C_{\text{Cu}} = \frac{31775}{18850.35}$$

$$= 1.68 \text{ mass\%}.$$

Using

$$C_{\text{Cu}} + C_{\text{Pt}} = 100$$

$$\begin{aligned} C_{\text{Pt}} &= 100 - C_{\text{Cu}} \\ &= 98.32 \text{ mass\%.} \end{aligned}$$

**Example 6**

What is the composition, in atom percentage, of an alloy that contains 33g of copper and 47g zinc.

$$A_{\text{Cu}} = 63.55 \text{ and } A_{\text{Zn}} = 65.41.$$

**Solution**

$$\text{at\%, } C'_i = \frac{n_{m_i}}{n_{m_1} + n_{m_2}} \times 100$$

$$\text{where } n_{m_1} = \frac{m'_1}{A_1} = \frac{33}{63.55}$$

$$n_{m_1} = 0.5193$$

$$n_{m_2} = \frac{m'_2}{A_2} = \frac{47}{65.41}$$

$$= 0.7185$$

$$C'_{\text{Cu}} = \frac{0.5193 \times 100}{0.5193 + 0.7185}$$

$$= \frac{51.93}{1.2378}$$

$$= 41.95 \text{ at\%}.$$

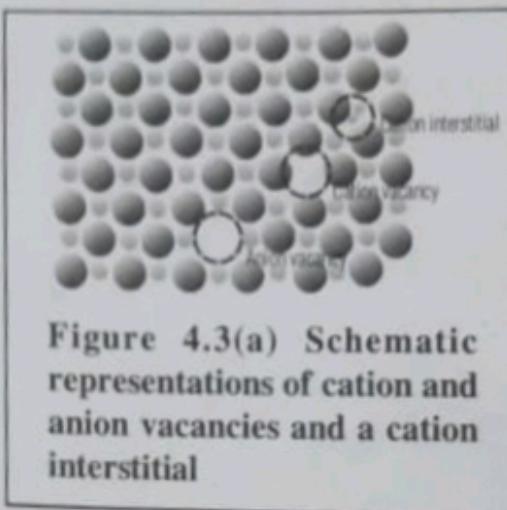
Using  $C'_{\text{Cu}} + C'_{\text{Zn}} = 100$

$$C'_{\text{Zn}} = 100 - 41.95$$

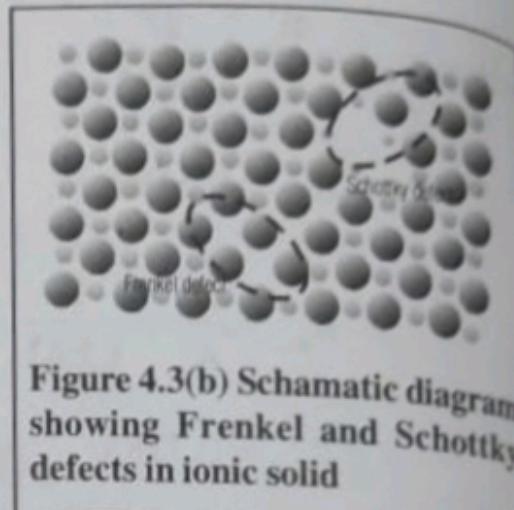
$$= 58.05 \text{ at\%}.$$

### Atomic pointdefects

Point defects are defects of zero dimensionality, i.e., they do not possess lattice structure in any dimension. In metals we found three point defects: vacancies, self interstitials and impurity atoms. Here we discuss point defects in ceramic compounds. Ceramic materials contain ions at atleast two kinds, defects of each type may occur. For example in NaCl, Na interstitials and vacancies and Cl interstitials and vacancies may occur. As the size of an ion is relatively large, the probability of occurrence of anion interstitials are very low. Thus we have only three types: Anion vacancy, cation varancy and cation interstitials. They are schematically represented in figure 4.3(a).



**Figure 4.3(a)** Schematic representations of cation and anion vacancies and a cation interstitial



**Figure 4.3(b)** Schematic diagram showing Frenkel and Schottky defects in ionic solid

There are three types of point defects found in ceramics. They are Frenkel defect, Schottky defect and nonstoichiometric defect.

### Frenkel defect

**Frenkel defect is formed when a cation leaving its normal position and moving into an interstitial site.**

When this defect occurs there is no change in charge because the cation maintains the same positive charge as an interstitial. See figure 4.3(b).

### Schottky defect

The defect occurs when a cation and an anion removed from the interior of the crystal and placing them both at an external surface. As a result a pair of cation vacancy – anion vacancy is formed. This is known as Schottky defect.

Here also the neutrality of the charge is maintained, since cations and anions have the same charge and for every anion vacancy there exists a cation vacancy. See figure 4.3(b).

It may be noted that the ratio of cations to anions is not altered by the formation of either a Frenkel defect or a Schottky defect. If no other defects are present the material is said to be stoichiometric.

## Stoichiometry

It is defined as a state for ionic compounds where in there is the exact ratio of cations to anions.

For example NaCl is stoichiometric if  $\frac{\text{Na}^+}{\text{Cl}^-} = 1$ . If there is any deviation from this it is known as nonstoichiometric.

## Nonstoichiometric defect

Any deviation from the ratio of cation and anion equal to one results in a defect known as nonstoichiometric defect.

This defect occurs in some of the ceramic materials in which two valence states exist for one of the ion types. Iron oxide (FeO) is one such material. Fe exists in both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  states. The number of each of these depends on temperature and the oxygen pressure. The formation of  $\text{Fe}^{3+}$  ion disrupts the electroneutrality of the crystal by introducing an excess +1 charge, which must be offset by some type of defect. This may be accomplished by the formation of one  $\text{Fe}^{2+}$  vacancy for every two  $\text{Fe}^{3+}$  ions are formed. The crystal is no longer stoichiometric because there is one more O ion than Fe ion. However the crystal remains electrically neutral. The nonstoichiometric defect indicates a deficiency of Fe. Thus chemical formula for iron oxide is written as  $\text{Fe}_{1-x}\text{O}$ , where x is some small and variable fraction less than one.

The equilibrium number of both Frenkel and Schottky defects that can occur in a crystal can be calculated by using

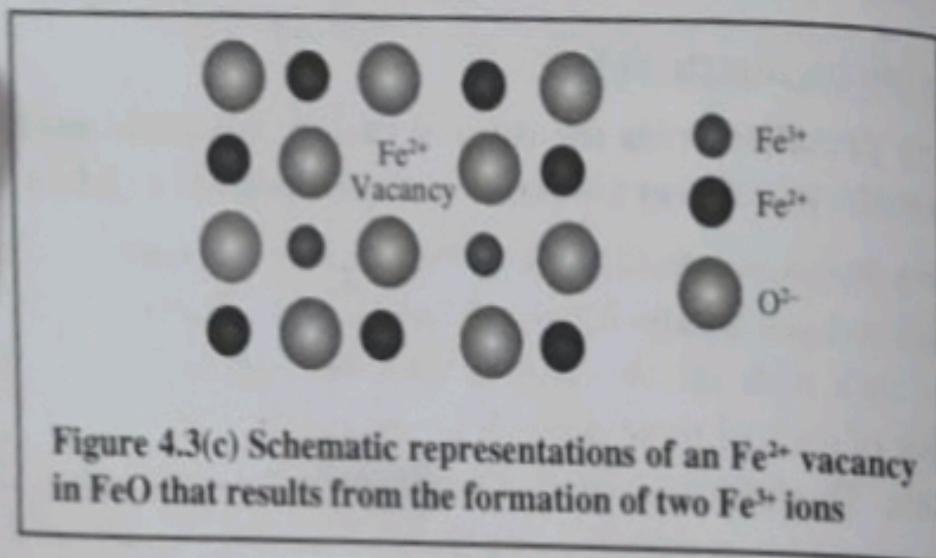
$$N_{fr} = N e^{\frac{-E_{fr}}{2kT}} \quad \dots\dots (18)$$

$N_{fr}$  is the number of cation vacancy / cation interstitial defect pairs, N is the total number of lattice sites and  $E_{fr}$  is the energy required for the formation of each Frenkel defect. Similarly for Schottky defect.

$$N_s = N_A e^{\frac{-E_s}{2kT}} \quad \dots\dots (19)$$

The number of sites in a metal,

$$N = \frac{N_A \rho}{A_{\text{metal}}}.$$



### Example 7

Calculate the number of Schottky defects per cubic metre in potassium chloride at 500°C. The energy required to form each Schottky defect is 2.6eV and density of KCl at 500°C is 1.955 gcm<sup>-3</sup>

$$A_K = 39.10 \text{ g/mol}$$

$$A_{\text{Cl}} = 35.45 \text{ g/mol}.$$

### Solution

The equilibrium number of Schottky defects,

$$N_s = N_A e^{\frac{-E_s}{2kT}} \quad \dots\dots (1)$$

$$E_s = 2.6 \text{ eV}$$

$$k = 8.62 \times 10^{-5} \text{ eV/K}$$

$$T = 500 + 273 = 773 \text{ K}$$

$$\rho = 1.955 \times 10^3 \text{ kg m}^{-3}$$

Number of lattice sites,

$$N = \frac{\rho N_A}{A_K + A_{Cl}}$$

$$N = \frac{1.955 \times 10^3 \times 6.023 \times 10^{23}}{39.10 \times 10^{-3} + 35.45 \times 10^{-3}}$$

$$N = 1.58 \times 10^{28} \text{ lattice sites per m}^3.$$

$$N_s = 1.58 \times 10^{28} \times e^{\frac{-2.6}{2 \times 8.62 \times 10^{-5}}} \times 773$$

$$N_s = 5.31 \times 10^{19} \text{ defects m}^{-3}.$$

### Example 8

Calculate the number of Frenkel defects per cubic metre in silver chloride at 350°C. The energy for defect formation is 1.1eV and the density of AgCl is 5.50 g cm<sup>-3</sup> at 350°C.  $A_{Ag} = 107.87 \text{ g/mol}$  and  $A_{Cl} = 35.45 \text{ g/mol}$ .

### Solution

The equilibrium number of Frenkel defects,

$$N_{fr} = N e^{\frac{-E_f}{2kT}} \quad \dots\dots (1)$$

$$E_f = 1.1 \text{ eV}$$

$$k = 8.62 \times 10^{-5} \text{ eV K}^{-1}$$

$$T = 350 + 273 = 623 \text{ K}$$

$$\begin{aligned} \frac{E_f}{2kT} &= \frac{1.1}{2 \times 8.62 \times 10^{-5} \times 623} \\ &= 10.24 \end{aligned} \quad \dots\dots (2)$$

$$e^{\frac{E_h}{kT}} = e^{-10.24} = 3.53 \times 10^{-5}$$

The number of lattice sites,

$$N = \frac{\rho N_A}{A_{Ag} + A_{Cl}}$$

$$\rho = 5.50 \times 10^3 \text{ kgm}^{-3}$$

$$A_{Ag} = 107.87 \times 10^{-3} \text{ kgmol}^{-1}$$

$$A_{Cl} = 35.45 \times 10^{-3} \text{ kgmol}^{-1}$$

$$N = \frac{5.50 \times 10^3 \times 6.023 \times 10^{23}}{107.87 \times 10^{-3} + 35.45 \times 10^{-3}}$$

$$N = \frac{5.50 \times 6.023 \times 10^{29}}{107.87 + 35.45}$$

$$N = \frac{33.1265 \times 10^{29}}{143.32}$$

$$N = 2.311 \times 10^{28} \text{ lattice sites per m}^3$$

$$N_{fr} = 2.311 \times 10^{28} \times 3.57 \times 10^{-5}$$

$$= 8.25 \times 10^{23} \text{ defects/m}^3$$

## Dislocations

We found that point defects are the irregularities or deviations from ideal arrangement around a point or an atom in the crystalline material.

**Dislocations are the irregularities or deviations from ideal arrangement in entire row of lattice points.**

Dislocations are called line defect since the defects are found

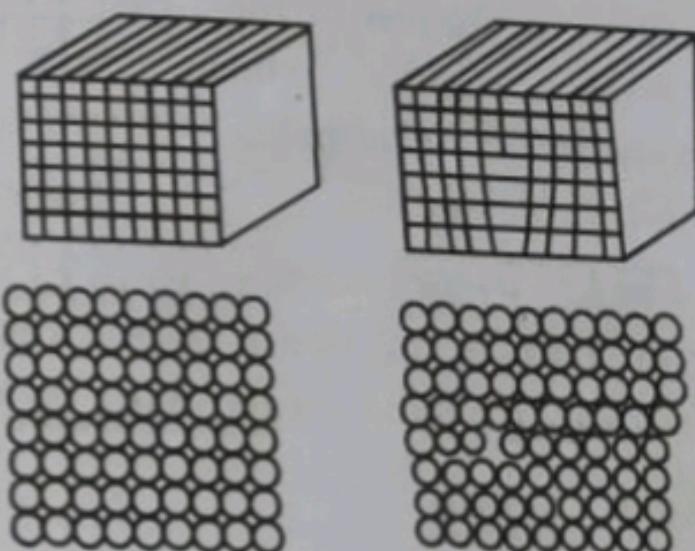
in a line. So it is a one dimensional imperfection. There are two basic types of dislocations: The edge dislocation and screw dislocation. Mixed dislocations, combining aspects of both types, are also common.

### Edge dislocation

An edge dislocation is a defect where an extra half-plane of atoms is introduced midway through the crystal, distorting nearby planes of atoms.

Figure 4.4(a) shows a perfect crystal, the top figure showing a three dimensional view and the bottom one showing the atoms on the front face. A perfect crystal is considered to be made up of vertical planes parallel to one another and to the side faces. If one of these vertical planes does not extend from the top to the bottom of the crystal but ends partway within the crystal, as shown in figure 4.4(b), a dislocation is present.

In a perfect crystal, the atoms are in equilibrium positions and all the bond lengths are in equilibrium value. In an imperfect crystal on the right (figure 4.4(b)). The edge of the incomplete plane, the atoms are squeezed and are in a state of compression. The bond lengths have been compressed to smaller than the equilibrium value. Just below the edge, the atoms are pulled apart and are in a state of tension. The bond lengths have been stretched to above the normal values. The distorted configuration extends all along the edge into the crystal. Thus as the region o



An incomplete plane in a crystal results  
in an edge dislocation

Figure 4.4(a)

Figure 4.4(b)

maximum distortion is centred around the edge of the incomplete plane, this distortion represents a line imperfection and is called an edge dislocation.

### Screw dislocation

Screw location is the defect of a crystal that results from a displacement of the atoms in one part of a crystal relative to the rest of the crystal, forming a spiral ramp around the dislocation line.

A screw dislocation is depicted in figure 4.5.

The figure shows what happens when one part of the crystal is displaced relative to the rest of the crystal and the displacement terminates within the crystal.

The row of atoms marking the termination of the displacement is the screw dislocation. EF indicates the dislocation line.

### Burger's vector

The Burger's vector is a vector which indicates how much and in what direction the lattice above the slip plane has been shifted with respect to the lattice below the slip plane.

The Burgers vector is perpendicular to the edge dislocation. It is  $\vec{ab}$  shown in figure 4.6(b).

In screw dislocation, the Burger's vector lies parallel to the dislocation line along the axis of a line of atoms in the same plane. In the figure 4.5, vector  $\vec{ab}$  is the Burger's vector.

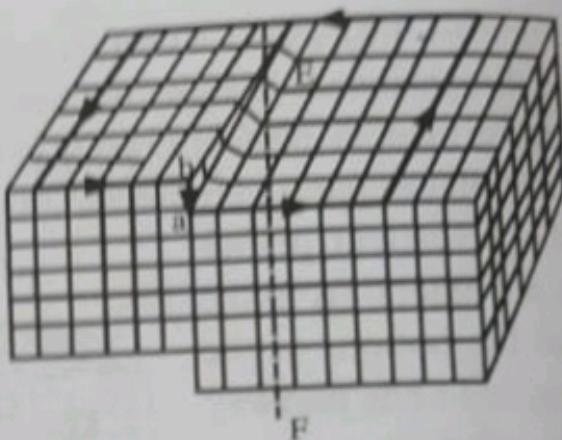


Figure 4.5: Screw dislocation

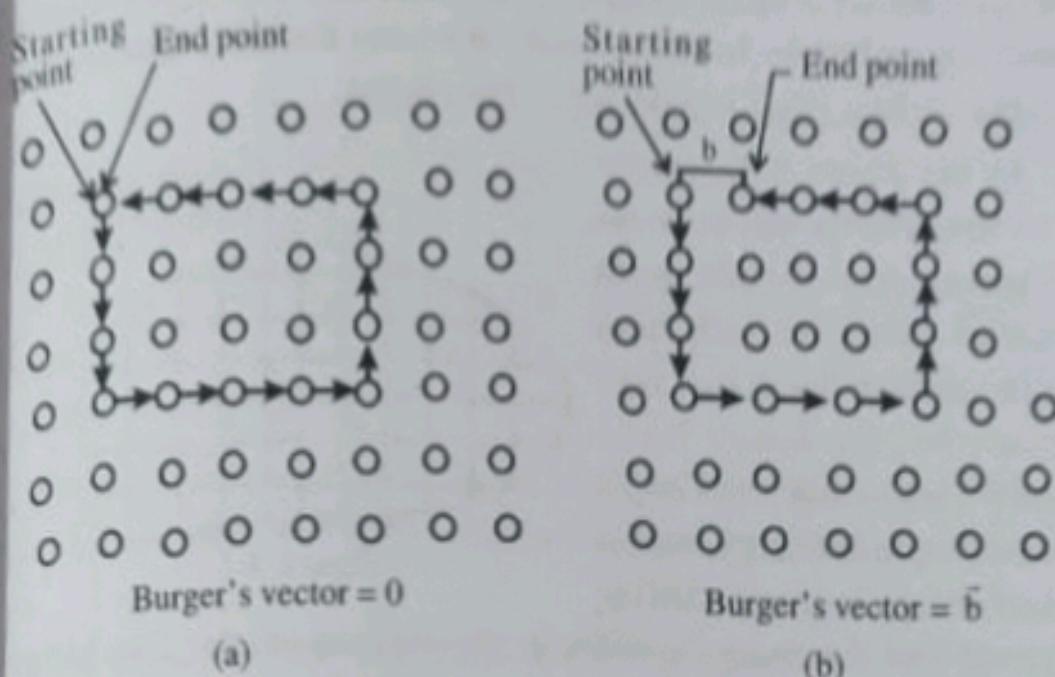


Figure 4.6: Burger's vector

## Interfacial defects

In the last section, we dealt with line defects. Now we discuss planer defects of crystals.

Planar defect (surface defect) is a discontinuity of a perfect crystal structure across a plane.

**Interfacial defects are boundaries that have two dimensions and normally separate regions of the materials that have different crystal structures and / or crystallographic orientations.**

Interfacial defects exist at an angle between two faces of a crystal. These imperfections include external surfaces, twin boundaries, grain boundaries, stacking faults and phase boundaries.

## External surface defect

One of the most obvious boundaries is the external surface along which crystal structure terminates. Since all the crystals are of finite sizes, so there will be always an external surface of that crystal and this external surface itself a kind of defect. Or at the surfaces

the periodicity of the crystal is disrupted. External surface leads to breaking of bonds. In other words it breaks the lattice periodicity so the surface itself is a defect in the crystal.

In the figure 4.7, we can see that every inside atom forming four bonds with nearest atoms but each atom at the surface has not all four bonds but the bonds break and we know that breaking of bonds requires energy, so that extra energy is provided to the crystal and the energy resides in the surface atoms. The higher energy of the surface atoms is called surface energy of the crystal. This is called external surface defect

### Grain boundary (defect)

**Grain boundaries** surface defect which separate crystals or grains of different orientation in a poly crystalline during crystallization or grain boundaries are the **region of orientations mismatch**. The shape of the grain is usually influence by the presence of surrounding grains. As a result, grain on one side of the boundary is rotated with respects the other side of the boundary grain. So

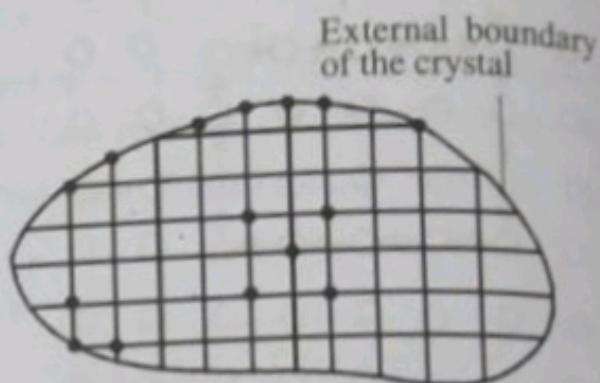


Figure 4.7

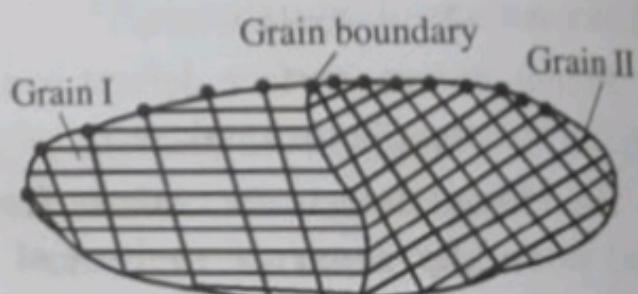


Figure 4.8

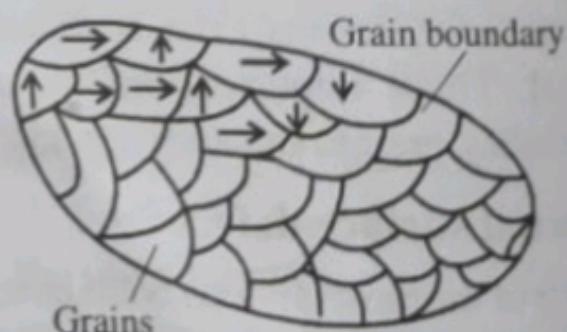


Figure 4.9: Poly crystal grain boundary

there is a rotation and the rotation is represented by a rotation axis and a rotation angle.

Classification of grain boundary is based on the magnitude of angle of rotation. There are two types. They are:

### 1. Small angle boundary

If the angle of rotation is small ( $< 5^\circ$ ) called small angle boundary.

### 2. Large angle boundary

If the angle of rotation is large ( $> 5^\circ$ ) called large angle boundary. There is another classification based on the relationship of rotation axis.

They are (1) Tilt boundary (2) Twist boundary.

If the rotation axis is parallel to the boundary is called tilt boundary. If the rotation axis is perpendicular to the boundary is called twist boundary. See figures below.

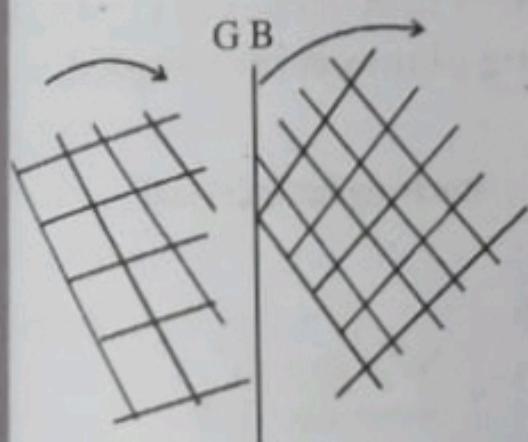


Figure 4.10(a): Tilt boundary

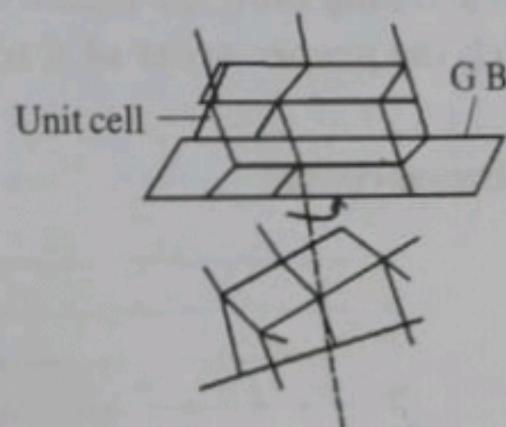


Figure 4.10(b): Twist boundary

### Twin boundaries

It is a boundary in a crystal such that crystals on either side are mirror images of each other.

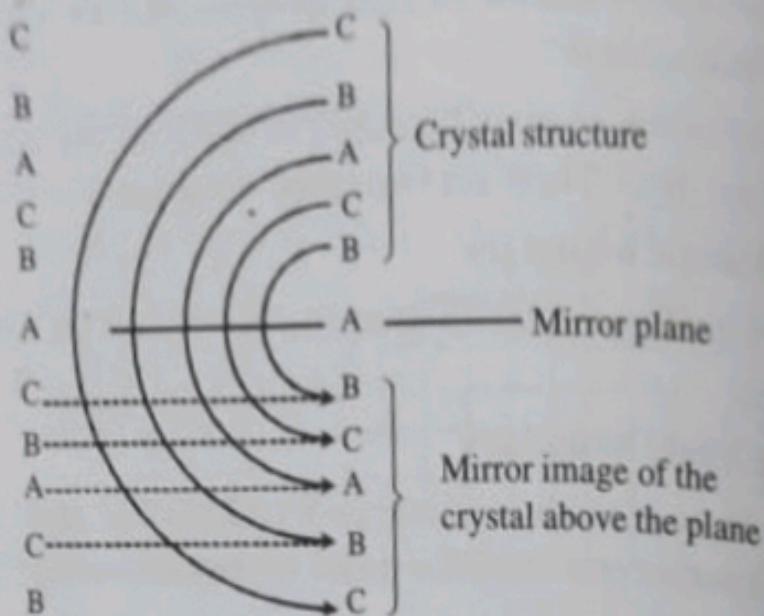


Figure 4.11: Twin boundary

### Stacking faults

It is a fault in the stacking sequence of a crystal.

A stacking fault is a planar defect that occurs in crystals in which the proper order of stacking planes is interrupted.

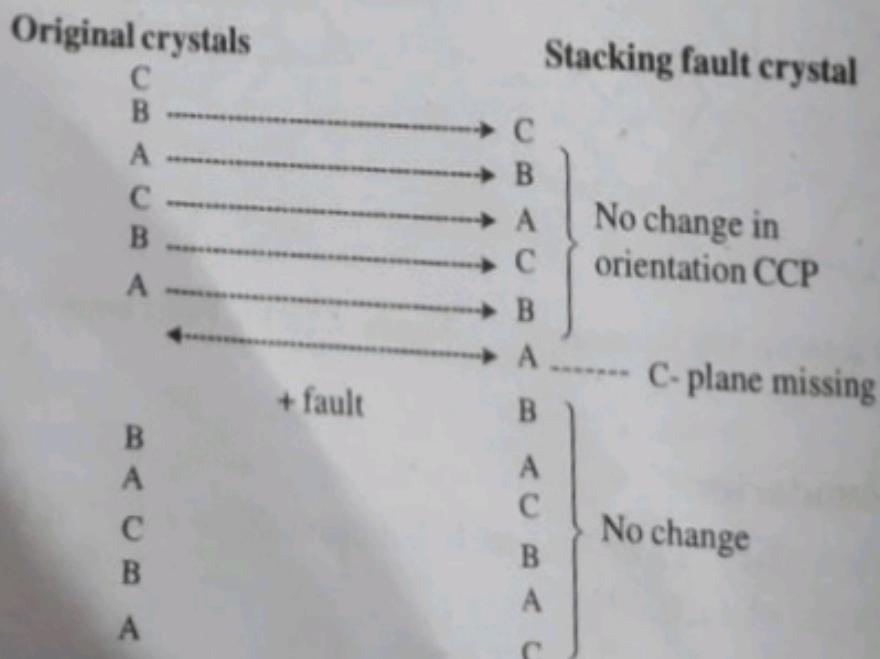


Figure 4.12: Stacking fault

Consider a crystal whose arrangement is CBACBACBA ..... suppose one of the C-plane is missing (see figure 4.12). As a result of this missing C-plane the sequence of arrangements above the C-plane is translated down. However the arrangements below the C-plane is unaltered. This defect is called stacking fault.

### Bulk or volume defects

**Bulk or volume defects are three dimensional imperfections that occur in a crystal.**

The volume defects are created by precipitates. Volume defects include voids, pores, cracks and foreign inclusions in crystalline materials. Pores can occur when a cluster of point defects combine together to form a three dimensional imperfection. This type of defect has a tremendous effect on the performance of materials.

Cracking arise when there is only small electrostatic dissimilarity between the stacking sequence of close packed planes in metals.

Foreign particles inclusions create large voids or non-crystalline regions which have the dimensions of at least 1 to 3nm are also called volume imperfections. When clusters of atoms are missing, a large vacancy or void is created which is also a volume imperfection.

### Effects of crystal imperfection

1. The addition of impurities (making imperfections) in the case of semiconductors increases the electrical conductivity. But in the case of metals it decreases the electrical conductivity.
2. The colour of a crystal is due to the selective absorption of some component of the visible spectrum by certain imperfections are called colour centres which are present in the crystal. These imperfections may be interstitial impurity atoms such as transition metal ions. Alternatively, they may be vacancies in the structure produced by deviations from stoichiometry so that there are present excess positive ions accom-

panied by negative vacancies or excess negative ions accompanied by positive vacancies. Thus when excess Zn is present in ZnO it takes a yellow colour. Excess lithium in LiF turns the crystal red. Excess potassium in KCl makes the crystal appear violet.

3. The imperfections account for
  - (i) flow and future characteristics.
  - (ii) crystal growth.
  - (iii) diffusion mechanisms.
  - (iv) creep characteristics of real metals and alloys.
  - (v) annealing and precipitation.
  - (vi) oxidation and corrosion.
  - (vii) yield strength, fracture strength plasticity, thermal conductivity, dielectric strength etc.
4. The defects influence the properties of the solids in the following different ways.
  - (i) The defects may scatter conduction electrons in a metal, increasing its electrical resistance by several percent in many pure metals and much more in alloys.
  - (ii) Some defects, even if present sparingly, decrease the strength of the crystal.
  - (iii) Pure salts having impurities and imperfections are often coloured.
  - (iv) Hysteresis loss of ferromagnets.
5. Imperfections do not always affect the properties of materials adversely. There are many situations in which controlled amount of imperfection can bring about specific characteristics desired in a crystal. For example carbon steel is a material whose properties are improved by imperfections in the cubic crystal structure of iron, increase the mechanical strength of iron.

## UNIVERSITY MODEL QUESTIONS

### Section A

**(Answer in two or three sentences)**

#### **Short answer type questions**

1. What is meant by the term imperfection in crystals?
2. Why the study of defects in crystals are important?
3. Classify the crystal defects on the basis of geometry.
4. Which are the point defects?
5. What is the effect of presence of vacancies in a crystal?
6. Write down an expression for the equilibrium number of vacancies in a crystal and explain the symbols used.
7. What is the effect of selfinterstitials in crystals?
8. Draw a schematic representation of a vacancy and a selfinterstitials.
9. What is solid solution? Mention two of its types.
10. Mention two features affecting the degree to which solute dissolves in solvent.
11. What is substitutional solid solution?
12. How does valency of metals influence in the formation of substitutional solid solution?
13. How does interstitial solution form?
14. Give an example of interstitial solid solution.
15. Give the schematic representations of substitutional and interstitial impurity atoms.
16. What is meant by the term "composition" of alloys?
17. Define the term "mass percent" in alloys.
18. Define the term "atom present" in alloys.
19. Write down the conversion formula from mass percent to atom percent and explain the symbols used.
20. Mention three point defects in crystals.